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Syntheses, Structures and Coordination Modes of Acetatopalladium(II) Complexes with 1,3-Bis(2-arylimino)isoindoline Ligands of Different Steric Influence

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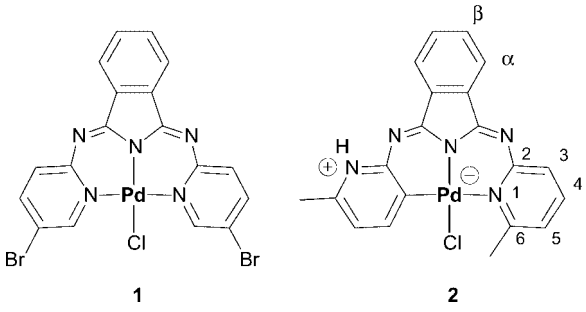
Keywords: Cyclometalation / Isoindoline ligands / Polynuclear complexes / Palladium / Coordination modes

Acetatopalladium(II) complexes of four different 1,3-bis(2-arylimino)isoindoline ligands (bai's) with different degrees of steric congestion have been prepared and were characterized by NMR and XRD with respect to nuclearity and coordination mode. In particular, the propensity for heteroaryl ring rotation and C–H activation has been investigated. Palladium(II) ions bind to bai ligands in different coordination modes, either as classical Werner-type *N*,*N*,*N* bonded complexes or—after pyridyl ring rotation and C–H activation—as carbometalated *C*,*N*,*N* chelates. In the latter case two (bai•)-Pd(OAc) subunits have been found to dimerize via two bridging Pd(OAc) moieties in the solid and in solution. These stable and electroneutral tetranuclear species are of low solubility in non-donor solvents, but break up into soluble dinuclear species of unknown composition upon the addition of DMSO, azide or cyanide. Attempts to activate C–C bonds by this strategy were not successful. Surprisingly, the exchange of the terminal pyridines by pyrimidines does not result in the formation of oligonuclear or oligomeric species. Besides the degree of steric hindrance, three more factors, solubility of the products, stoichiometry of metal precursor and charge compensation, have been identified to govern the outcome of the metalation of these bai ligands.

Introduction

Palladacycles[1] constitute an important class of organometallic species. Despite their historical role in the development of organometallic chemistry,[2] cyclometallated palladium(II) compounds have found entry in many different fields like organic synthesis, catalysis, and material science.[3] In addition, many of the nowadays indispensable palladium-promoted organic transformations are considered to proceed via palladacyclic intermediates.[4]

1,3-Bis(2-arylimino)isoindolines (bai) are monoanionic, meridonal tridentate *N*,*N*,*N* ligands[5] that were first introduced in the 1950s.[6] Palladium(II) complexes of such bai ligands like **1** and others are known as classical coordination compounds,[7] and their catalytic capabilities in the hydrogenation of alkenes have been demonstrated.[8] In a recent study it was described that steric strain applied to the coordination unit of such classical (bai)Pd complexes by well-situated terminal methyl groups results in an intriguing reactivity, i.e. pyridine ring rotation and C–H activation of the heteroaromatic ligand, to yield the carbopalladated 1,3-bis(6-methylpyridyl-2-imino)isoindoline (6-Me-bpi*) species **2** (Figure 1).[9] This report tempted us to investigate the reactivity of palladium(II) ions on bai ligands of different steric influence and to compare their behaviour with a class of related meridonal-tridentate *N*,*N*,*N* ligands, the α,ω-dimethyltripyrrins,[10] that we had studied before. In a first attempt we were able to show, that the stoichiometry of the palladium precursor added to the bai ligand is responsible for the outcome of the reaction, i.e. the formation of a Werner-type or a cyclopalladated product, if the steric hindrance is equal for the N- and the C donor positions.[11] We have now extended the study to ligands with different degrees of intramolecular strain, and report here about the results of our work.



1 **2**

Figure 1. *N*,*N*,*N* vs. *C*,*N*,*N* binding mode of unstrained and strained (bpi)PdCl derivatives **1**[7a)] and **2**.[9]

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Results and Discussion

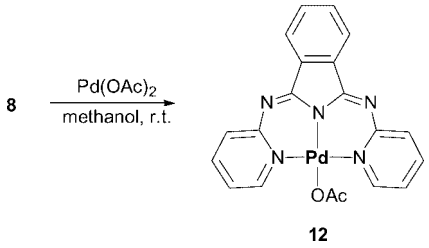
Preparation of 1,3-Bis(2-arylimino)isoindolines H(bai) 8–11

The preparation of the 1,3-bis(2-arylimino)isoindolines H(bai) **8**–**11** used in this study is presented in Scheme 1. In general, symmetric H(bai) derivatives can be prepared by a method introduced by Siegl[5a)] upon treatment of phthalodinitrile **3** with a heteroarylamine $ArNH_2$ **4**–**7** and calcium chloride in 1-butanol (Scheme 1). **8** and **9** had been prepared by this approach before.[5a] The new compounds **10** and **11** form in yields of 62% and 7%, and were analyzed by elemental analyses and HRMS, respectively. The low yield was obtained for H(4-Me-bpmi) **11** after 7 d at reflux and is a result of the fair reactivity of aminopyrimidine **7**. Only one successful attempt for the preparation of H(bpmi) derivatives had been described in literature so far.[5j]

The interpretation of the spectroscopic properties of **10** and **11** is straightforward and proofs that the new derivatives behave very similar to other known H(bai) species.[5a)] The NMR spectra show C_{2v} symmetric species in solution and are typically governed by the large number of signals arising from the different aromatic C–H groups. These congested spectra can easily be interpreted after separation in three subspectra. The signals of the methyl group protons typically appear between δ = 2 and 3 ppm (2.42 and 2.43 ppm for **10**, 2.58 ppm for **11**). The second subspectrum concerns the α- and β protons of the central C_6H_4 moiety, which lead to two multiplets for **10** and **11** at 8.05/7.65 and 8.10/7.68 ppm, respectively. The other signals at 7.46/6.86 ppm and 8.62/6.96 ppm belong to the C–H protons of the terminal heterocycles, i.e. the pyridines in **10** and the pyrimidines in **11**. A similar signal pattern is also found for all (bai)Pd^{II}(OAc) complexes in this study. For the free base ligands **10** and **11**, however, another broad signal indicating a NH function appears at δ = 12.3 and 13.3 ppm, respectively.

Formation of Mono- and Tetranuclear Species 12 and 13 from H(bai) 8 and 9

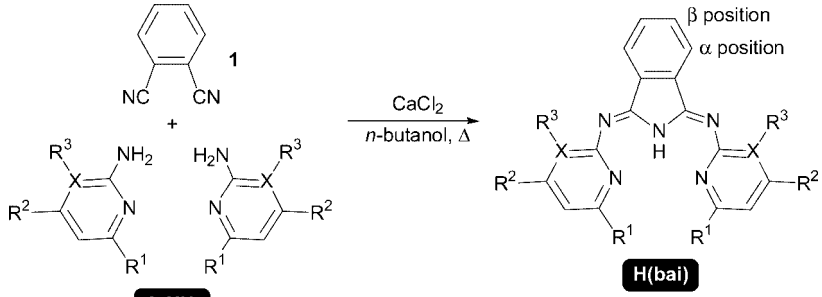
The complex (bpi)Pd(OAc) **12** was prepared from 1,3-bis(pyridyl-2-imino)isoindoline H(bpi)[5a)] (**8**) and palladium acetate in methanol and precipitates from the reaction mixture as an orange, microcrystalline powder in a yield of 76% (Scheme 2). The constitution $C_{20}H_{15}N_5PdO_2$ was confirmed by combustion analysis and MALDI-MS.



Scheme 2. Preparation of (bpi)Pd(OAc) **12**.

^1H and ^{13}C NMR spectra of **12** are in agreement with a compound of C_2 symmetry. The acetato ligand can be detected by characteristic signals for the methyl protons and for the carbon atoms at 2.15, 24.8 and 172.7 ppm, respectively. The assumed Werner-type *N*,*N*,*N* coordination of the palladium ion was established by a X-ray crystallographic analysis. A suitable crystal (CH_2Cl_2 solvate) grew from a dichloromethane solution at –40 °C. Selected bond lengths and angles are summarized in Table 1 (with Figure 2). Table 2 gives crystallographic details. The molecular structure of **12** is shown in Figure 3.

The molecular structure of **12** confirms the solution spectra and shows a palladium(II) ion coordinated to three nitrogen atoms N1, N2 and N3 of the bpi ligand at distances of 2.038(5), 1.946(5) and 2.037(5) Å. The fourth coordination site is occupied by the O1 donor atom of the acetate moiety in a distance of 2.034(3) Å. The central Pd–N2 bond is markedly shorter than the other two. Literature proposes



	$ArNH_2$	H(bai)
X = C; R^1,R^2,R^3 = H	**4**	**8**
X = C; R^1 = Me; R^2,R^3 = H	**5**	**9**
X = C; R^1,R^3 = Me; R^2 = H	**6**	**10**
X = N; R^1 = Me; R^2,R^3 = H	**7**	**11**

Scheme 1. Preparation of H(bai) ligands **8**–**11**.

Table 1. Selected structural data for **12**, **13**, **14** and **15**.[a]

Compound	**12**	**13**	**14 A**[b]	**14 B**[b]	**15**
N1–Pd1	2.038(5)	2.174(7)	2.083(4)	2.070(4)	2.048(2)
N2–Pd1	1.946(5)	1.987(9)	1.949(4)	1.954(4)	1.958(2)
N3–Pd1/C*–Pd1	2.037(5)	1.975(9)	2.080(4)	2.090(4)	2.060(2)
O1–Pd1	2.034(3)	2.054(7)	2.053(3)	2.045(3)	2.033(2)
N3–Pd2	–	2.010(9)	–	–	–
N5–Pd2	–	2.079(8)	–	–	–
O2–Pd2	–	2.029(7)	–	–	–
O3–Pd2	–	1.977(6)	–	–	–
N1–Pd1–N2	89.87(19)	90.1(3)	89.15(15)	89.98(15)	89.31(10)
N1–Pd1–N3/C*	169.29(19)	170.3(3)	164.71(14)	166.81(14)	178.81(10)
N1–Pd1–O1	91.27(17)	92.7(3)	90.36(12)	89.33(12)	92.27(9)
N2–Pd1–N3/C*	89.91(19)	90.6(4)	90.20(16)	90.36(16)	89.80(10)
N2–Pd1–O1	174.58(17)	169.6(3)	160.27(14)	160.66(14)	177.59(9)
N3/C*–Pd1–O1	89.94(17)	88.4(3)	95.34(13)	94.66(13)	88.60(9)
N3–Pd2–N5	–	65.0(3)	–	–	–
N3–Pd2–O2	–	173.3(3)	–	–	–
N3–Pd2–O3	–	101.4(3)	–	–	–
N5–Pd2–O2	–	108.3(3)	–	–	–
N5–Pd2–O3	–	166.3(3)	–	–	–
O2–Pd2–O3	–	85.2(3)	–	–	–

[a] Unified numbering scheme used for all compounds, see Figure 2. [b] A and B correspond to distinct molecules in the unit cell.

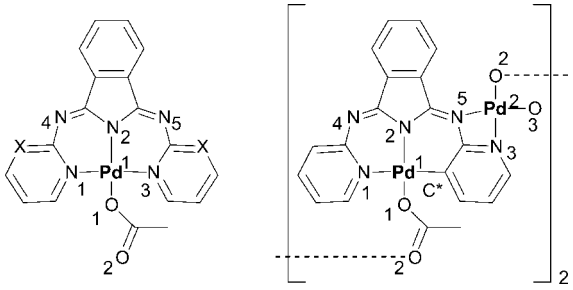


Figure 2. Unified numbering scheme adapted for use in crystallographic determinations.

the increased ionic character of this bond to be responsible for this observation[7a)] that is due to a largely localized negative charge at N2. The deviation of the angles N1–Pd–

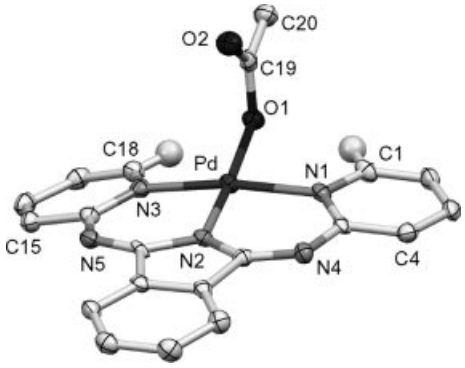


Figure 3. Molecular structure of (bpi)Pd(OAc) **12** in the solid state (most hydrogen atoms omitted for clarity; ellipsoids are set at the 50% probability level).

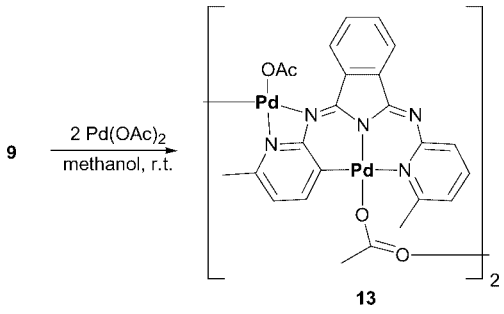
Table 2. Crystallographic details.

Compound	**12**×CH_2Cl_2	**13**	**14**	**15**×$CHCl_3$
Formula	$C_{21}H_{17}Cl_2N_5O_2Pd$	$C_{24}H_{21}N_5O_4Pd_2$	$C_{24}H_{23}N_5O_2Pd$	$C_{21}H_{18}Cl_3N_7O_2Pd$
M_r /g mol^{-1}	548.70	656.26	519.87	613.17
Space group	$P2_1/n$	$C2/c$	Pn	$P2_1/n$
a /Å	12.0777(12)	15.442(3)	12.0930(11)	14.0418(14)
b /Å	10.9337(11)	17.764(4)	12.8156(11)	8.1576(6)
c /Å	16.0578(19)	18.220(4)	14.3969(13)	20.894(2)
β /°	103.415(13)	97.69(3)	107.903(10)	103.288(12)
V /Å^3	2062.6(4)	4953.0(17)	2123.2(3)	2329.3(4)
Z	4	8	4	4
$d_{calcd.}$ /g cm^{-3}	1.767	1.760	1.626	1.749
Crystal size /mm^3	0.48 × 0.24 × 0.12	0.23 × 0.19 × 0.05	0.20 × 0.16 × 0.12	0.46 × 0.11 × 0.04
μ(Mo-K_α) /mm^{-1}	1.189	1.492	0.907	1.176
2θ limits /°	4.0–51.8	4.0–50.4	4.36–51.96	3.96–52.12
Measured reflections	15071	7808	16264	17818
Independent reflections	3648	4232	8067	4525
Observed reflections[a]	2781	2368	7015	3242
No. parameters	281	320	588	338
R_1[b] (R_1 all data)	0.0683	0.0988	0.0331	0.0485
wR_2[c] (wR_2 all data)	0.1384	0.1509	0.0531	0.0697
Max. / min. peaks	1.788 / –1.497	1.937/ –1.445	0.592/–0.408	0.609/–0.461

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}1/2$.

N3 and N2–Pd–O1 of 10.7° and 5.4°, respectively, from 180° reveal a non-planar coordination of the d^8 Pd^{II} ion that obviously derives from steric interactions between the acetato donor O1 and the terminal protons at C1,18. With 2.208 and 2.212 Å the O1···H distances are found to undercut the van der Waals limit by up to 15.1%.[12] For **1** and **2** which contain the larger chlorido ligand instead of the acetate oxygen atom the N2–Pd–Cl angle is found steeper at 167.74 and 165.13°, respectively, but with a similar degree of X···H and/or X···CH_3 interaction of 16.3–20.2% below the van der Waals limit. The bpi ligand of **12** displays a non-planar, convex conformation with twists of the pyridyl and isoindole ring mean squares planes from the N1,N2,N3 plane of 10.82°, 14.42° and 4.34°, respectively. Similar twists are unknown for related tripyrrin complexes and allow bai ligands to better adapt to coordinative requirements by a higher degree of conformational flexibility.

The reaction of H(6-Me-bpi) **9** with two equivalents of palladium(II) acetate also proceeds under the slow formation of a solid precipitate. The product **13** that is obtained after filtration and excessive washing with methanol in 46% yield, however, shows a lower solubility and an entirely different constitution than (bpi)Pd(OAc) **12**. From mass spectra and combustion analytical data the presence of a tetranuclear dimer can be concluded. As will be shown by XRD and NMR studies the constitution of the product **13** is that of a carbopalladated tetranuclear dimer as displayed in Scheme 3. **13** forms very selectively even if less than the stoichiometric amount of palladium acetate is used, and it is reasonable to assume that the low solubility of the tetranuclear dimer efficiently supports the selective formation of the unexpected product. A similar behaviour has been observed with the 4,6-Me2-bpi derivative,[11] if two (or more) equivalents of palladium acetate are employed.



Scheme 3. Formation of [(6-Me-bpi*)$_2$Pd$_4$(OAc)$_4$] **13**.

A crystal of **13** suitable for a X-ray crystallographic analysis was obtained from a solution in chloroform by layering with *n*-hexane and diffusion at room temperature. **13** crystallizes as a solvate, presumably a dihydrate, in the monoclinic system, space group *C*2/*c*, with $Z = 8$. Due to the severe disorder the solvent was removed using the SQUEEZE command in PLATON. The molecular structure of **13** contains two identical monomeric subunits and is presented in Figure 4. Selected bond lengths and angles are given in Table 1. Table 2 summarizes crystallographic details.

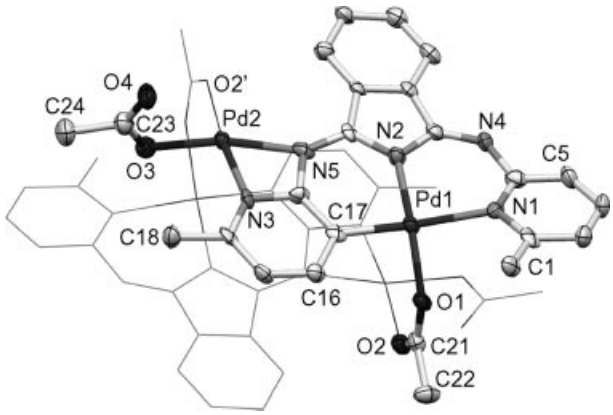


Figure 4. Molecular structure of (6-Me-bpi*)$_2$Pd$_4$(OAc)$_4$ **13** in the solid state (hydrogen atoms omitted for clarity; ellipsoids are set at the 50% probability level).

Complex **13** is a dimer of a palladium complex of a C-H activated 6-Me-bpi ligand, referred to as 6-Me-bpi*. The monomeric (6-Me-bpi*)Pd$_2$(OAc) subunits are doubly bridged by two bidentate acetato ligands which occupy one coordination site on each type of palladium ion, the central ion Pd1 and the peripheral ion Pd2, with Pd–O distances of 2.054(7) and 2.029(7) Å. Besides the acetate coordination the peripheral Pd^{II} ion is bound to N3 and N5 in distances of 2.010(9) and 2.079(8) Å, respectively, and with a narrow N3–Pd2–N5 angle of 65.0(3)°. The fourth coordination site of the distorted square-planar Pd2 ion is saturated by a terminal acetate in a distance of 1.977(6) Å. The *C*,*N*,*N* coordination of the Pd1 atom of **13** is identical to the one recently reported for the mononuclear H[(6-Me-bpi*)PdCl] **2**.[9] Instead of a second palladium ion coordinated to N3 and N5, however, **2** contains a proton at N3 for charge balance. For this reason as well as for the geometrical differences of the bridging coordination modes of chlorido vs. acetato ligands precedent **2** lacks the ability for dimerization via intermolecular coordinative interactions and thus remains monomeric. With the exception of nuclearity, however, the metrics of **2** and **13** as determined by XRD are very similar.

The (6-Me-bpi*)Pd subunits of **13** are stacked above each other in an antiparallel orientation and in a distance of about 3.157 Å. The correlation (Pd–N1) > (Pd–N2) seen above for the Werner-type complex **12** is retained in **13**, and the *trans* influence of the C* donor opposite to N1 is clearly visible in the elongated Pd–N1 bond of 2.174(7) Å. The carbon atom C17 of the inverted pyridine moiety binds to Pd1 in a distance of 1.975(7) Å. The conformation of the 6-Me-bpi* ligand is convex as in **12** but unsymmetric in the predictable sense that the *N* bound pyridine ring with the methyl group close to the acetate O1 atom shows a large tilt of 18.82° while the *C* bonded pyridine ring with the methyl group turned away from the acetato ligand tilts only slightly by 9.78° with respect to the N1,N2,C* plane. The distances O1···H16 and O1···CH_3 of 2.362 and 2.764 Å are 9.2% and 18.7% below the van der Waals limit and therefore again in a range that appears typical for this class of

compounds. With the exception of the remaining rotational freedom of the terminal acetates the tetranuclear and dimeric morphology of **13** is very rigid, so that the poor solubility of this compound can be rationalized from its structure.

The ^{1}H NMR spectrum of **13** in CD_2Cl_2 shows a characteristic signal at δ = 5.51 ppm that was assigned to a proton situated at the C–H activated pyridyl residue (H5) by H,H COSY spectroscopy (see ESI, Figure S1). As the molecular structure of **13** reveals, this proton is situated directly above the aromatic C_6H_4 moiety of the isoindoline subunit of the symmetry equivalent monomer in a distance of about 3.3 Å. The high field shift observed for this signal is a consequence from the aromatic ring current of the benzene moiety, and H5 can thus be regarded a probe for the degree of aggregation. The ^{1}H NMR spectra proof that the dimeric nature of **13** is not broken up in non-donor solvents like CH_2Cl_2 but largely resemble those found in the solid state. The XRD and NMR results of **13** resemble those observed before for a related 4,6-Me_2-bpi derivative.[11]

Investigations of the Formation and Deaggregation of the Tetranuclear Species 13

While for **9** only the tetranuclear cage compound **13** could be isolated in substance, it was possible to isolate a Werner-type complex like **11** with the 4,6-Me_2-bpi ligand, depending on the stoichiometry of the metallation agent.[11] Obviously, the steric hindrance for C–H activation is higher for the 4,6-Me_2-bpi complex and leads to an increased kinetic stabilization of a mononuclear Werner-type species. In order to gain insight into the elemental steps of the formation of **13** the reaction between H(6-Me-bpi) **9** and two equivalents of $Pd(OAc)_2$ was carried out in deuterated methanol and investigated by ^{1}H NMR spectroscopy. The mixture became turbid after a hour, and a spectrum was recorded which clearly showed the presence of two major and one minor species (Figure 5). One of the major as well as the minor species could be identified as the free base ligand H(6-Me-bpi) **9** and as a tetranuclear dimer similar to or identical with **13**, which seems to be present already in its saturation concentration. The remaining signals indicate the presence of a new, C_2 symmetric compound with a higher solubility, presumably the Werner-type complex (6-Me-bpi)Pd(OAc). Unfortunately all attempts to isolate this species failed, and **13** was obtained after work-up as the sole product. The study shows that the pyridine rotation and the C–H activation step occur *after* the initial metalation of **9**, and that the kinetic stability of the Werner-type intermediate (6-Me-bpi)Pd(OAc) in the presence of excess Pd^{II} ions is not sufficient to prevent the concurring precipitation of **13**. With respect to the exclusive formation of the Werner-type compound from the unhindered ligand **8** this result supports the hypothesis of strain-induced C–H activation[9] and proofs the labilizing influence of steric strain on the kinetic stability of *N*,*N*,*N* bound species. Further insight into the C–H activation step and/or the pyridine ring inversion, however, could not be obtained. Especially the role of the solvent for the observed pyridin ring rotation/cyclometallation reaction remains unclear, since all attempts to metallate different bai ligands with palladium(II) acetate in solvents other than methanol yielded mixtures of several unassigned compounds.

A second set of ^{1}H NMR spectroscopic experiments was devoted to the deaggregation of **13** and the possible determination of the structures of dinuclear fragments of **13**. The experiments were carried out using a) a donor solvent ([D_6]-DMSO), b) a donor anion in a donor solvent (NaN_3 in [D_6]DMSO), and c) a donor anion in a non-donor solvent ([nBu$_4$N]CN in CD_2Cl_2; see ESI for selected details from ^{1}H-NMR and H,H-COSY spectra obtained from these experiments).

If the ^{1}H NMR spectrum of **13** is measured in [D_6]-DMSO a major compound with C_s symmetry and without signals for aromatic C–H groups below a chemical shift of 6.9 ppm is detected, indicating a monomeric species in solution. In addition, a number of poorly resolved signals appear and indicate the presence of several side products. An

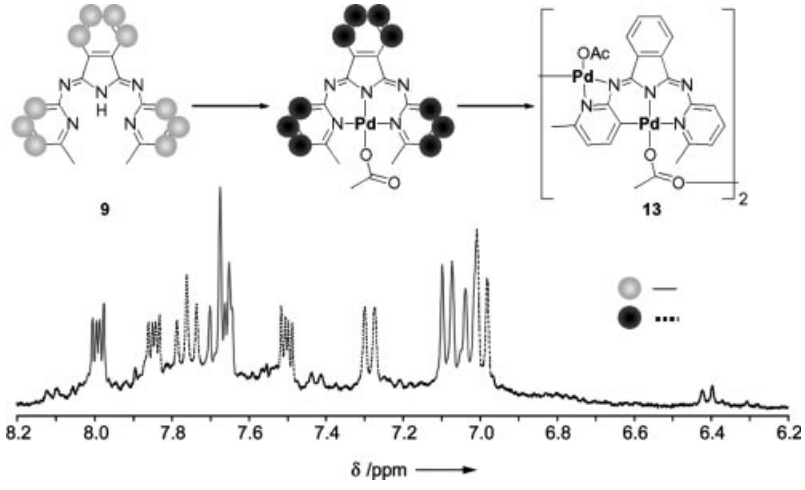


Figure 5. Details from the ^{1}H NMR spectroscopic reaction control of the metalation of **9** (400 MHz, [D4]MeOH) and identification of the Werner-type monomeric species (6-Me-bpi)Pd(OAc).

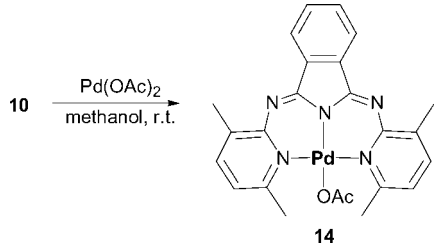
exact description of the molecular structure of the monomeric species, however, or a decision about whether one or two palladium ions are bound to the 6-Me-bpi* ligand, can not be given from the spectrum.

Upon the addition of excess sodium azide to the solution of **13** in [D_6]DMSO the spectrum clearifies and now displays the presence of one major and one minor compound which are both monomeric in nature and show both C_s symmetry (presumably isomers). In addition only one singlet for an acetate species is present at δ = 1.64 ppm. This value is characteristic for a weakly bound acetate (e.g. NaOAc in [D_6]DMSO: 1.57 ppm) and suggests complete exchange for azido ligands.

A similar ^{1}H NMR spectrum with a major and a minor form and a single signal for acetate protons at δ = 1.78 ppm was obtained from **13** in deuterated dichloromethane upon the addition of tetra-*n*-butylammonium cyanide. Directly after the addition a colour change from orange to yellow was observed. After several hours a yellow solid formed and precipitated from this solution. The solid is insoluble in most solvents, but is slowly taken up in pyridine with an intense yellow colour. The formation and reactivity of the insoluble final product may be explained by the polymerization of a dinuclear fragment [(6-Me-bpi*)Pd_2CN]$^+$ via μ-cyanido ligands.

Metalation Behaviour of New bai Ligands H(bai) 10 and 11

The ease of C–H activation promoted by a simple steric stimulation as in **13** tempted us to use the same stimulus for a C–C activation reaction. Similar reactions have been studied before in pincer complexes with other noble metals like ruthenium, iridium and others.[13] Towards this goal the suitably substituted H(3,6-Me_2-bpi) **10** was designed and employed in the reaction with palladium acetate under standard conditions (Scheme 4). Even upon prolonged heating, however, only the Werner-type complex **14** was formed and could be isolated in 21% yield. Elemental analysis and mass spectra confirmed the constitution $C_{24}H_{23}N_5O_2Pd$ of **14**.



Scheme 4. Preparation of (3,6-Me_2-bpi)Pd(OAc) **14**.

The C_2 symmetry of the product can be derived from the proton and carbon NMR spectra. Support for the assignments was obtained by a X-ray crystallographic analysis. Two similar molecules **A** and **B** are present in the unit cell of which only the parameters of molecule **A** will be discussed. The molecular structure of **14A** is shown in Figure 6. Selected bond lengths and angles for both molecules are summarized in Table 1. Table 2 gives crystallographic details for the structure determination.

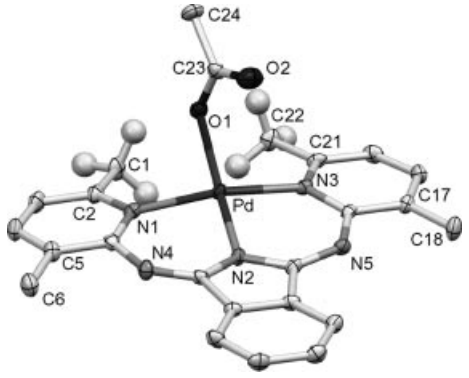


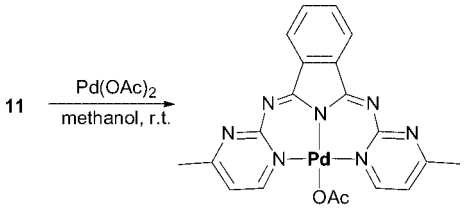
Figure 6. Molecular structure of (3,6-Me_2-bpi)Pd(OAc) **14** (molecule **A**) in the solid state (most hydrogen atoms omitted for clarity; ellipsoids are set at the 50% probability level).

The result from the crystallographic analysis of **14** shows the expected distortion of the coordination sphere of the palladium(II) ion by non-linear N1–Pd–N3 and N2–Pd–O1 angles of 164.71° and 160.27°, respectively. These angles correspond to a pseudoplanar conformation of the 3,6-Me_2-bpi ligand[10b)] and indicate repulsive interactions between the terminal methyl groups of the bpi subunit and the O1 donor atom of the acetate group. Other than the bpi ligand in **12**, however, the 3,6-Me_2-bpi ligand of **14** shows no convex distortion but rather a conformation, in which the mean squares plane of the isoindole subunit is about 0.3–0.5 Å underneath the (almost) coplanar mean squares plane of both pyridyl moieties. This arrangement results in additional space for the acetate O1 donor atom which is located in distances of 2.792(6) and 2.845(6) Å, i.e. 17.9% and 16.3% below the van der Waals limit, from the terminal methyl groups. Very similar values of 16.0% and 18.1% have been obtained from the related mononuclear (4,6-Me_2-bpi)Pd(OAc) described earlier.[11] In both cases, an additional fraction of intramolecular strain is distributed to the Pd–N1 and Pd–N3 bonds as judged by their elongations of about 0.04 Å with respect to **12**. Obviously, the system contains sufficient resources to compensate for intramolecular strain, so that a process that requires a significantly larger activation energy than the C(sp^2)–H activation is not sufficiently promoted by this approach.

Of particular interest was the question of why the C–H activation of **13** does not occur on the site of the peripheral Pd^{II} ion and without pyridyl ring rotation. In particular it is unclear, whether the pyridyl rotation/C–H activation step is necessary for the coordination of a second palladium ion (as could be suggested from the inertness of **12** towards additional $Pd(OAc)_2$), or if the coordination of a second ion (Pd^{II} for **13** and the 4,6-Me_2-bpi precedent, H^+ for **2**) to an initially formed kinetic product, i.e. the signals of a Werner-type *N*,*N*,*N*-bonded complex seen in the NMR experiment (Figure 5) or the isolated mononuclear 4,6-Me_2-bpi complex, assists in this process. To answer this question

the bis(pyrimidyl) derivative **11** was designed. The kinetic *and* the thermodynamic product of the reaction of **11** with a first equivalent of $Pd(OAc)_2$ must be identical due to the inability of **11** to undergo a C–H activation process, and should already exhibit two heteroaryl termini with two methyl groups and two *N* donor atoms pointing outwards. Thus, as the final product, a di- or trinuclear complex or an aggregate thereof should be expected.

11 was metalated under standard conditions and a new, yellow compound **15** separated from the reaction mixture (Scheme 5). Elemental analysis and mass spectra indicate the exclusive formation of a mononuclear compound. Surprisingly, neither a two- or threefold metalation nor a di- or oligomerization occurs despite the presence of excessive palladium acetate. ^1H and ^{13}C NMR spectroscopic data for **15** again suggests the formation of a C_2 symmetric species. Whether both methyl termini point in- or outwards could be clearified in favour of the latter scenario by a X-ray diffraction study.



15

Scheme 5. Preparation of (6-Me-bpmi)Pd(OAc) **15**.

Yellow needles of **15** suitable for the XRD investigation were obtained by diffusion of *n*-hexane into a $CHCl_3$ solution at room temperature. The molecular structure of **15** is shown in Figure 7. Selected bond lengths and angles are summarized in Table 1. Table 2 gives crystallographic details.

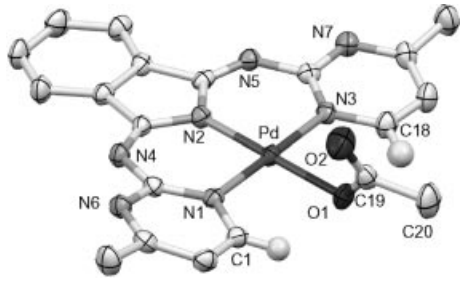


Figure 7. Molecular structure of (6-Me-bpmi)Pd(OAc) **15** in the solid state (most hydrogen atoms omitted for clarity; ellipsoids are set at the 50% probability level).

Complex **15** resides in the expected conformation for a mononuclear chelate, in that the methyl substituents of both pyrimidine rings point outwards. Other than for **12** the coordination environment of the Pd^{II} ion of **15** is close to planar, and the N1–Pd–N3– and N2–Pd–O1–angles are almost linear with 178.81(10)° and 177.59(9)°, respectively. Related values in the (trpy)Pd series usually indicate a *helical* conformation of the organic chelate ligand.[10a,10b,10f,10g] For **15** a new conformation, the concave twist (with respect to the orientation of the acetate group; Figure 7), is observed. With angles between mean squares planes of the pyrimidine(N1) and pyrimidine(N3) subunits and the N1,N2,N3 plane of only 11.06(15)° and 3.36(15)°, respectively, the heterocycles are only slightly tilted away. The Pd–N (1.958(2)–2.060(2) Å] and Pd–O1 distances (2.033(2) Å] are intermediate to those observed for the bpi complexes **12** and **14**, and the typical shortness of the Pd–N2 bond is observed for **15**, too. **15** is thus another example for the structural diversity of bai complexes.

Two rationals may be considered for the exclusive formation of a mononuclear and monomeric species in the reaction of **11** with palladium acetate. First, the outwards pointing methyl groups might interfere with the coordination of a second equivalent of the metal carrier, and secondly, **15** is devoid of a ionic trigger. The first argument appears improbable due to the fact that the same steric encumbrance is present at the peripheral coordination site of the tetranuclear dimer **13**. For the second, more probable argument one has to consider that the monomeric and mononuclear species from **13**, $[(6\text{-Me-bpi*})Pd(OAc)]^-$, which is the formal *C* bonded analog of **15**, carries a negative charge that promotes the binding of another cation.

Conclusions

In summary we have prepared a set of related (bai)-Pd^{II}(OAc) complexes and characterized them in solution and in the solid state with respect to their propensity for intramolecular C–H and C–C activation in dependence of intramolecular strain. In the majority of cases classical, though strained Werner type coordination compounds were found. Despite their constitution from sp^2 centres the bai ligands show a remarkable flexibility that allows to adapt smoothly to coordinative constraints and dissipates much of the strain energy to the ligand backbone. As a second coordination mode C–H activation has been observed in a tetranuclear dimer. This outcome of the metalation reaction appears feasible if the rotation of one pyridyl ring is sufficiently supported by the sterics. The comparative study with a pyrimidine derived ligand unraveled, that the binding of a second palladium(II) ion occurs most probably *after* the C–H activation step and becomes a favourable process mainly due to charge balance. Thus the second cation supports the selective formation of a cyclopalladated product mainly indirectly by the formation of a neutral dimer with a low solubility.

Experimental Section

General: All reagents and solvents were purchased from commercial sources. Reagents were used as received. Solvents were dried by standard methods and stored under an argon atmosphere. NMR spectra were obtained on a Bruker ARX 300 or DRX 400 spectrometer in the solvents indicated below. Mass spectra were recorded on a VG Tribid or a Varian CH7 (EI, 70 eV), a Bruker Biflex IV (MALDI), a Qstar Pulsar i (HR-MALDI) or a Ionspec Ultima (ESI) instrument. *m*/*z* values are given for the most abun-

dant isotopes only. UV/Vis spectra were measured on a Shimadzu UV1601PC in the range from 200–1100 nm. For X-ray crystallographic measurements an IPDS-I (Stoe) was used. All structures were solved using "*SHELXS*, Program for Crystal Structure Determination"[14] and refined with "*SHELXL*, Program for Crystal Structure Refinement".[15] The solvent in the structure of **13** was removed using the program SQUEEZE in PLATON.[16] CCDC-639805 to -639808 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Syntheses of 1,3-Bis(arylimino)isoindolines H(bai) 10 and 11. General Procedure: Phthalodinitrile (**1**) (2.56 g, 20 mmol), heterocyclic amine **6** or 7 (50 mmol) and anhydrous calcium chloride (0.22 g, 2 mmol) are suspended in 1-butanol and heated to reflux for 44 h (**10**) or 168 h (**11**). The solvent is removed in vacuo to leave a yellowish residue. For **10** this solid is extracted with dichloromethane, filtered and recrystallized by the addition of *n*-hexane to leave a yellow solid. For **11** chromatography on silica with THF/pentane (1:3, then 2:1), followed by recrystallization from THF/pentane (1:1) produces a clean, yellow material.

1,3-Bis(3,6-dimethyl-2-pyridylimino)isoindoline (10): Yield 4.40 g (62%), m.p. 140–142 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 2.42 (s, 6 H, CH_3), 2.43 (s, 6 H, CH_3), 6.86 (d, ^3J = 7.6 Hz, 2 H, 5-CH_{Py}), 7.46 (d, ^3J = 7.6 Hz, 2 H, 4-CH_{Py}), 7.62–7.68 (m, 2 H, β-CH), 8.02–8.07 (m, 2 H, α-CH), 12.3 (s br, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 17.2, 24.1, 119.5, 122.2, 126.9, 131.5, 136.0, 139.2, 151.8, 154.2, 158.2 ppm. MS (EI): *m*/*z* = 355 [M$^+$], 249 ([M – C_7H_8N]$^+$), 235 ([M – $C_7H_8N_2$]$^+$). UV/Vis (CH_2Cl_2): λ_{max} = 237, 286, 384 nm. $C_{22}H_{21}N_5$ (355.436): calcd. C 74.34, H 5.96, N 19.70; found C 74.18, H 5.82, N 19.43.

1,3-Bis(4-methyl-2-pyrimidinylimino)isoindoline (11): Yield 0.50 g (7%), m.p. >200 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 2.58 (s, 6 H, CH_3), 6.96 (d, ^3J = 5.1 Hz, 2 H, 5-CH_{Pm}), 7.67–7.70 (m, 2 H, β-CH), 8.08–8.12 (m, 2 H, α-CH), 8.62 (d, ^3J = 5.1 Hz, 2 H, 4-CH_{Pm}), 13.3 (s br, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 24.3, 116.5, 123.1, 132.5, 135.8, 156.4, 157.5, 165.1, 168.8 ppm. HRMS (ESI) calcd. for $C_{18}H_{15}N_7Na$: 352.1281; obs. 352.1281, Δ = 0.0 mmu. UV/Vis (CH_2Cl_2): λ_{max} = 265, 337, 350 nm.

Syntheses of Acetatopalladium(II) Chelates 12–15. General Procedure: H(bai) **8**–**11** (0.1 mmol) and palladium acetate (44.9 mg, 0.2 mmol) are suspended in methanol (3 mL) and stirred at ambient temperature under a blanket of argon for 16 h. A solid separates, which is collected by filtration and washed extensively with methanol to leave the product as a red to orange solid.

(bpi)Pd(OAc) 12: Yield 35.3 mg (76%), m.p. >200 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 2.15 (s, 3 H, OAc), 7.13 (t, ^3J = 6.3 Hz, 2 H, CH_{Py}), 7.55–7.98 (m, 4 H, CH_{Py}, α-CH), 7.58–7.63 (m, 4 H, CH_{Py}, β-CH), 8.89 (m, 2 H, CH_{Py}) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 24.8, 120.4, 122.4, 127.5, 131.7, 138.3, 139.7, 148.4, 152.1, 145.0, 172.7 ppm. MS (MALDI): *m*/*z* = 404 [[M – OAc]$^+$]. UV/Vis (CH_2Cl_2): λ_{max} = 241, 330, 434, 463 nm. $C_{20}H_{15}N_5O_2Pd$ (463.79): calcd. C 51.79, H 3.26, N 15.10; found C 51.60, H 3.25, N 15.07.

(6-Me-bpi*)$_2$Pd$_4$(OAc)$_4$ (13): Yield 30.2 mg (46%), m.p. >200 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.33 (s, 3 H, CH_3), 1.98 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 3.04 (s, 3 H, CH_3), 5.51 (d, ^3J = 8.3 Hz, 1 H, 5-CH_{Py}), 7.10 (d, ^3J = 7.6 Hz, 1 H, CH'_{Py}), 7.15 (d, ^3J = 8.3 Hz, 1 H, 1 H, 4-CH_{Py}), 7.32 (m, 1 H, β/β′-CH), 7.43 (d, ^3J = 7.3 Hz, 1 H, CH'_{Py}), 7.51 (m, 1 H, β/β′-CH), 7.67 (d, ^3J = 8.0 Hz, 1 H, α/α′-CH), 7.76 (t, ^3J = 7.6 Hz, 1 H, 4-CH'_{Py}), 7.87 (d, ^3J = 7.3 Hz, 1 H, α/α′-CH) ppm. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.78 (s, 2 H), 1.91 (s, 2 H), 1.99 (s, 2 H), 2.87 (s, 3 H, CH_3), 3.19 (s, 3 H, CH_3), 6.94 (d, ^3J = 6.6 Hz, 1 H, CH_{Py}), 7.14 (d, ^3J = 7.3 Hz, 1 H, CH'_{Py}), 7.38 (d, ^3J = 8.0 Hz, 1 H, CH'_{Py}), 7.68–7.76 (m, 2 H, β,β′-CH), 7.87 (t, ^3J = 6.5 Hz, 1 H, CH'_{Py}), 8.02 (d, ^3J = 7.3 Hz, 1 H, α/α′-CH), 8.13 (d, ^3J = 6.6 Hz, 1 H, CH_{Py}), 9.13 (d, ^3J = 6.6 Hz, 1 H, α/α′-CH), 11.94 (br.s, 1 H) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 19.3, 21.9, 25.4, 26.2, 116.6, 118.1, 121.9, 122.5, 123.8, 124.0, 128.4, 130.9, 134.2, 138.3, 144.4, 154.9, 160.0, 182.3; due to the low solubility of the compound the signals for two quarternary carbon atoms were not detected ppm. MS (MALDI): *m*/*z* = 1253 ([M – OAc]$^+$), 598 ([M/2 – OAc]$^+$), 432 ([(6-Me-bpi*)Pd]$^+$). UV/Vis (CH_2Cl_2): λ_{max} = 237, 306, 359, 458, 489 nm. $C_{48}H_{42}N_{10}O_8Pd_4$ (1312.59): calcd. C 43.92, H 3.23, N 10.67; found C 43.70, H 3.43, N 10.53.

(3,6-Me$_2$-bpi)Pd(OAc) (14): Yield 10.9 mg (21%), m.p. >200 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 1.76 (s, 3 H, OAc), 2.59 (s, 6 H, CH_3), 2.60 (s, 6 H, CH_3), 6.84 (d, ^3J = 7.6 Hz, 2 H, CH_{Py}), 7.51–7.56 (m, 2 H, β-CH), 7.57–7.92 (m, 2 H, α-CH), 7.59 (d, ^3J = 7.3 Hz, 2 H, CH_{Py}) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 25 °C): δ = 17.8, 23.5, 26.8, 121.3, 122.2, 129.6, 130.9, 137.7, 140.2, 152.6, 154.7, 159.2, 176.7 ppm. HRMS (ESI) calcd. for $C_{22}H_{20}N_5Pd$: 460.0754; obs. 460.0757, Δ = 0.3 mmu. UV/Vis (CH_2Cl_2): λ_{max} = 240, 376, 505, 537 nm. $C_{24}H_{23}N_5O_2Pd$ (519.89): calcd. C 55.45, H 4.46, N 13.47; found C 54.88, H 4.30, N 13.39.

(6-Me-bpmi)Pd(OAc) (15): Yield 35.6 mg (72%), m.p. >200 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.12 (s, 3 H, OAc), 2.65 (s, 6 H, CH_3), 6.99 (d, ^3J = 6.2 Hz, 2 H, *5*-CH_{Pm}), 7.60–8.63 (m, 2 H, β-CH), 8.15–8.18 (m, 2 H, α-CH), 8.87 (d, ^3J = 6.2 Hz, 2 H, *4*-CH_{Pm}) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 24.5, 24.6, 116.4, 123.5, 132.3, 137.6, 154.9, 156.1, 160.2, 172.0, 177.9 ppm. MS (MALDI): *m*/*z* 434 ([M – OAc]$^+$). HRMS (MALDI) calcd. for $C_{18}H_{14}N_7Pd$: 434.0345; obs. 434.03437, Δ = 0.2 mmu. UV/Vis (CH_2Cl_2): λ_{max} = 344, 420, 444 nm. $C_{20}H_{17}N_7O_2Pd{\cdot}CHCl_3$ (613.19): calcd. C 41.13, H 2.96, N 15.99; found C 41.09, H 2.90, N 16.14.

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[1] J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2572.

[2] a) A. C. Cope, R. W. Siekman, *J. Am. Chem. Soc.* **1965**, *87*, 3272–3273; b) A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909–913.

[3] a) G. W. Parshall, *Acc. Chem. Res.* **1970**, *3*, 139–144; b) J. Dehand, M. Pfeffer, *Coord. Chem. Rev.* **1976**, *18*, 327–358; c) M. I. Bruce, *Angew. Chem.* **1977**, *89*, 75–89; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 73–86; d) I. Omae, *Chem. Rev.* **1979**, *79*, 287–321; e) I. Omae, *Coord. Chem. Rev.* **1982**, *42*, 245–257; f) E. C. Constable, *Polyhedron* **1984**, *3*, 1037–1057; g) G. R. Newkome, W. E. Puckett, V. K. Gupta, G. E. Kiefer, *Chem. Rev.* **1986**, *86*, 451–489; h) M. Pfeffer, *Pure Appl. Chem.* **1992**, *64*, 335–342; i) P. Steenwinkel, R. A. Gossage, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 759–762; j) W. A. Herrmann, V. P. W. Bohm, C. P. Reisinger, *J. Organomet. Chem.* **1999**, *576*, 23–41; k) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; l) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917–1927; m) R. B. Bedford, *Chem. Commun.* **2003**, 1787–1796; n) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792;

o) R. B. Bedford, C. S. J. Cazin, D. Holder, *Coord. Chem. Rev.* **2004**, *248*, 2283–2321; p) I. Omae, *Coord. Chem. Rev.* **2004**, *248*, 995–1023; q) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082.
[4] G. Dyker, *Chem. Ber./Recueil* **1997**, *130*, 1567–1578.
[5] a) W. O. Siegl, *J. Org. Chem.* **1977**, *42*, 1872–1878; b) F. A. Chavez, P. K. Mascharak, *Acc. Chem. Res.* **2000**, *33*, 539–545; c) O. P. Anderson, A. la Cour, A. Dodd, A. D. Garrett, M. Wicholas, *Inorg. Chem.* **2003**, *42*, 4513–4515; d) E. Balogh-Hergovich, G. Speier, M. Réglier, M. Giorgi, E. Kuzmann, A. Vértes, *Eur. J. Inorg. Chem.* **2003**, 1735–1740; e) M. B. Meder, L. H. Gade, *Eur. J. Inorg. Chem.* **2004**, 2716–2722; f) M. B. Meder, B. A. Siggelkow, L. H. Gade, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1962–1968; g) E. Balogh-Hergovich, G. Speier, M. Réglier, M. Giorgi, E. Kuzmann, A. Vértes, *Inorg. Chem. Commun.* **2005**, *8*, 457–459; h) M. Wicholas, A. D. Garrett, M. Gleaves, A. M. Morris, M. Rehm, O. P. Anderson, A. La Cour, *Inorg. Chem.* **2006**, *45*, 5804–5811. Other coordination modes have occasionally been reported, see for example i) D. M. Baird, K. Y. Shih, J. H. Welch, R. D. Bereman, *Polyhedron* **1989**, *8*, 2359–2365; j) D. M. Baird, K. Y. Shih, *Polyhedron* **1991**, *10*, 229–235; k) O. P. Anderson, A. la Cour, A. Dodd, A. D. Garrett, M. Wicholas, *Inorg. Chem.* **2003**, *42*, 122–127.
[6] a) J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1952**, 5000–5007; b) J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1952**, 5008–5015; c) P. F. Clark, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.* **1953**, 3593–3602.
[7] a) B. A. Siggelkow, M. B. Meder, C. H. Galka, L. H. Gade, *Eur. J. Inorg. Chem.* **2004**, 3424–3435; b) M. Meder, C. H. Galka, L. H. Gade, *Monatsh. Chem.* **2005**, *136*, 1693–1706; c) B. A. Siggelkow, L. H. Gade, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2575–2584; d) M. B. Meder, I. Haller, L. H. Gade, *Dalton Trans.* **2005**, 1403–1415.
[8] B. A. Siggelkow, M. B. Meder, C. H. Galka, L. H. Gade, *Eur. J. Inorg. Chem.* **2004**, 3424–3435.
[9] B. L. Dietrich, J. Egbert, A. M. Morris, M. Wicholas, O. P. Anderson, S. M. Miller, *Inorg. Chem.* **2005**, *44*, 6476–6481.
[10] a) M. Bröring, C. D. Brandt, *Chem. Commun.* **2001**, 499–500; b) M. Bröring, C. D. Brandt, *J. Chem. Soc. Dalton Trans.* **2002**, 1391–1395; c) M. Bröring, C. D. Brandt, *Chem. Commun.* **2003**, 2156–2157; d) M. Bröring, C. D. Brandt, S. Stellwag, *Chem. Commun.* **2003**, 2344–2345; e) M. Bröring, C. D. Brandt, S. Link, *Inorg. Chim. Acta* **2005**, *358*, 3122–3134; f) M. Bröring, S. Prikhodovski, C. D. Brandt, E. Cónsul Tejero, *Z. Anorg. Allg. Chem.* **2007**, *633*, 458–464; g) M. Bröring, S. Prikhodovski, S. Köhler, *Acta Crystallogr., Sect. C* **2007**, *63*, m68–m70.
[11] M. Bröring, C. Kleeberg, *Dalton Trans.* **2007**, 1101–1103.
[12] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
[13] See e.g.: a) B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, *111*, 918–932; *Angew. Chem. Int. Ed.* **1999**, *38*, 870–883; b) M. Gandelman, A. Vigalok, L. Konstantinovsky, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 9848–9849; c) R. M. Gauvin, H. Rozenberg, L. J. W. Shimon, D. Milstein, *Organometallics* **2001**, *20*, 1719–1724; d) B. Rybtchinski, S. Oevers, M. Montag, A. Vigalok, H. Rozenberg, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2001**, *123*, 9064–9077.
[14] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Determination*, University of Göttingen, **1997**.
[15] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, **1997**.
[16] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C-34.

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